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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in or relating to Method of Producing a Stably Tacky Eucohesive Pressure-sensitive Adhesive and the Pressure-sensitive Adhesive resulting from said method.

We, MINNESOTA MINING AND MANUFACTURING COMPANY, a Corporation of the State of Delaware, United States of America, of 900, Fauquier Avenue, City of St. Paul, State of Minnesota, United States of America, (Assignees of Clarence J. Ebel), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to aggressively and stably tacky adhesives useful in pressure-sensitive adhesive tapes: and to tapes having backings coated therewith. Such adhesive tapes are normally tacky and seal instantly on application without the need of moistening or heating. They are used for masking, sealing packages, mending books and records, and fastening posters on window panes and bulletin boards, for example. The tape can be removed from smooth surfaces to which temporarily applied without leaving a residue of adhesive, and can be handled without gumming the fingers. The tape is ordinarily supplied in rolls and these can be unwound without transfer or off-setting of adhesive.

In accordance with the present invention there is provided a method of producing a stably tacky eucohesive pressure-sensitive adhesive useful in adhesive tapes which comprises heating a sub-rubbery butadiene-styrene co-polymer with an oil-soluble heat-advancing phenol-aldehyde resin or a self-vulcanizing organic accelerator of the thiuram-polysulfide type to a stage at which the product is more cohesive than adhesive but still tacky, the product being substantially free from after-vulcanization and tack-loss at room temperatures.

[Prior

The present invention also provides a normally and stably tacky eucohesive pressure-sensitive adhesive tape consisting of a backing coated or impregnated with an adhesive comprising a sub-rubbery butadiene-styrene co-polymer which has been heated with an oil-soluble heat-advancing phenol-aldehyde resin or a self-vulcanizing organic accelerator of the thiuram-polysulfide type which is more cohesive than adhesive but stably tacky at room temperatures, and which is substantially free from after-vulcanization and tack-loss at room temperatures.

The expressions "vulcanization", "vulcanizing" and "vulcanized" as used herein are intended to mean heating a sub-rubbery butadiene-type polymer or copolymer with (a) an oil-soluble heat-advancing rubber reactive phenol formaldehyde type of resin or (b) a self-vulcanizing organic accelerator of the thiuram-polysulfide type.

Pressure-sensitive tape adhesives have commonly been formed of a water-insoluble blend of a rubbery base and a compatible tackifier resin, which may also contain modifiers, such as pigments and plasticizers. A natural or synthetic rubber base provides cohesion (internal strength) and elasticity (a retractive force when stretched and retraction when released after stretching). The compatible tackifier resin increases adhesion (tackiness) and decreases cohesion, with an attendant modification of stretchiness (elongation under low stresses) and elasticity; thereby resulting in an adhesive having a proper four-fold balance of adhesion, cohesion, stretchiness and elasticity. It is this four-fold balance which permits the tape to be aggressively and stably tacky and yet capable

of being stripped back from smooth non-fibrous surfaces to which temporarily applied (such as those of plate glass, metal sheets, and packaging films) without delamination or offsetting of adhesive, even though the adhesive is coated upon a glassy-surfaced non-porous film backing having approximately the same adhesion value toward it. These adhesives are termed "eucohesive" by which it is meant that they are more cohesive than adhesive such that offsetting or transfer of adhesive material does not result when a tape coated therewith is unwound from rolls or removed from surfaces to which temporarily applied, and can be handled without transfer of adhesive material to the fingers.

Thus it is evident that pressure-sensitive tape adhesives involve a balanced combination of physical properties and that it is not enough to merely provide a sticky material.

This invention provides a pressure-sensitive tape adhesive having desirable properties not found in the prior art rubber-resin adhesives and, unlike such adhesives, it is not made from natural or synthetic rubber modified by a tackifier resin.

We have discovered that synthetic butadiene-styrene sub-rubbery intermediate copolymers, which are inherently sticky but are pasty or fluid masses having inadequate cohesion and elasticity for direct use as pressure-sensitive tape adhesives, may be heat-vulcanized to obtain stably tacky eucohesive pressure-sensitive tape adhesives having a proper four-fold balance of adhesion, cohesion, stretchiness and elasticity. Thus, we have discovered that vulcanization can be used to increase cohesion and elasticity to the necessary degree without at the same time producing a transformed state which lacks the aggressive tackiness and the stretchiness which are needed for the intended use. The extent of vulcanization is controlled so as to avoid a transformation to a non-tacky or inadequately tacky state, and a vulcanizing agent is used which will not cause substantial after-vulcanization and tack-loss at normal temperatures. A feature of the adhesive is that it is substantially non-thermoplastic, in contrast to the ordinary rubber-resin type adhesives which soften and ooze when tapes coated therewith are subjected to elevated temperatures. An excess of vulcanizing agent does not cause loss of tack at normal temperatures but serves to film-up the adhesive still further when the tape is subjected to elevated temperatures. The adhesive is non-staining when applied to light-colored enamels (such as enamels on stoves and refrigerators) even on long contact and even when heated. The adhesive has excellent aging properties and a high resistance to mineral oils and waxes. Adhe-

sives can be made which are non-corrosive to copper and have other qualities which are highly desirable in electrical tapes used in the manufacture of radio coils and the like.

The pressure-sensitive tape adhesives of this invention may be applied to the usual backing sheet materials employed in making tape, such as cloths, unified papers (flat or creped), and non-fibrous films. Excellent transparent tapes can be made by coating a transparent non-fibrous film backing (such as cellophane Registered Trade Mark) with transparent adhesive; and such tapes are superior for permanent mending of books and records.

Butadiene-styrene sub-rubbery intermediate co-polymers may be prepared by emulsion polymerization of the starting monomers under conditions which prevent polymerization to the rubbery state which would otherwise result; followed by coagulation, washing and drying. The polymer may be a co-polymer, such as a co-polymer of butadiene and styrene. The term "sub-rubbery" means that the monomeric starting material was potentially capable of being polymerized to a rubbery material (as distinguished from a hard or brittle material), but was not permitted to produce copolymers of sufficient chain length, the polymerization being stopped at an intermediate pasty stage. The coagulated sub-rubbery polymer material is sticky and in-elastic, and may vary from a syrupy liquid to a plastic, which is less cohesive than adhesive. It may be termed a "pasty rubber", since it is broadly similar to what is obtained by breaking down a rubbery polymer to a pasty state in which the polymer chains have a reduced length.

The polymer material may be given a "thumb test" to show its physical state. The material is allowed to stand at room temperature for 24 hours if in a recently worked or heated condition. A small mass is taken between thumb and forefinger, which are alternately separated and brought together several times. If it is in the rubbery stage it will transfer from finger to finger and be substantially non-tacky. If in the sub-rubbery or pasty stage, it will stick to both fingers and can be drawn out until it finally splits, showing that it is less cohesive than adhesive. If the sub-rubbery polymer has been vulcanized in accordance with this invention, it will be quite tacky and yet will pull clean from the fingers without splitting, showing that it is eucohesive.

These sticky sub-rubbery co-polymer masses contain individual polymer chains of varying lengths. When vulcanized as herein set forth, to produce eucohesive pressure-sensitive tape adhesives, there is apparently produced a gel matrix of vulcanized longer molecules which provides a highly cohesive

and elastic body within which is dispersed a sol phase of the shorter molecules which make for aggressive tackiness and increased stretchiness. At any rate, the vulcanized complex has properties quite different from what would be obtained if the mass were more fully vulcanized, since vulcanization of the sticky sub-rubbery mass can be carried to the point of producing a non-tacky product having little stretchiness.

The sub-rubbery butadiene-styrene polymers are reactive to vulcanizing agents as hereinbefore referred to capable of vulcanizing the rubbery polymers which the starting monomers would form if permitted to do so.

The effect of vulcanization is not only to increase cohesion and apparent elasticity, and to decrease stretchiness and tackiness, but to decrease thermoplasticity and solubility.

The use of tackifier resins is not required in order to make pressure-sensitive tape adhesives in accordance with this invention. However, such resins may be included as modifiers in order to increase the degree of tackiness and produce a more vicious, resinous, type of grab. Plasticizers and softeners may be included. Zinc oxide, whiting, clay and carbon black can be incorporated as reinforcing agents or fillers. Coloring pigments can be incorporated.

PREPARATION OF SUB-RUBBERY CO-POLYMERS

The following illustrates a method of preparing a suitable sub-rubbery co-polymer of butadiene and styrene by an emulsion polymerization procedure. The initial monomeric emulsion has the formulation given below (but does not include the last two items):

	Parts by Weight
Butadiene	75
Styrene	25
Emulsifier (fatty acid soap)	4.6
Stabilizer	1.0
(such as "Daxad (Registered Trade Mark) 11", sold by Dewey & Almy Chemical Co.)	
Catalyst (potassium persulfate)	1.0
Chain terminator (dodecyl mercaptan)	2.0
Water	160
Shortstop (hydroquinone-added at end of reaction)	0.25
Antioxidant (added to finished latex)	2.0
(such as "Stalite", sold by R. T. Vandervilt Co.).	

Heat the emulsion at a moderately elevated temperature, e.g. about 120° F., and with continuous agitation, for approximately 10—12 hours, i.e. until a test sample shows a total solids content of approximately

33%. Add the hydroquinone "shortstop" to prevent further polymerization. Remove unreacted butadiene and styrene, together with a small amount of water, by distillation, finishing the distillation under reduced pressure. Add the antioxidant to the finished cooled latex; which is coagulated, washed and dried to yield the finished sub-rubbery co-polymer.

The "chain terminator" (illustrated by dodecyl mercaptan) functions to prevent the polymer chains from growing beyond a reduced length which is less than the length needed for rubbery polymers. The "short-stop", added at the end of the desired reaction period, neutralizes the effect of the catalyst and prevents subsequent further polymerization.

In a typical example, using butadiene of 97.8% and styrene of 99.0% purity, the "shortstop" was added and polymerization stopped after 10½ hours at 122° F., at which time the solids content of the emulsion was 30.8%. After removal of the residual non-polymerized monomers, the solids content was found to be 33.3%.

The dry sub-rubbery co-polymer was obtained by coagulation followed by washing and drying. A portion was tested for viscosity, using an Ostwald type capillary tube viscosimeter calibrated with pure toluene. The co-polymer was tested as a 1.01% solution in toluene. The following figures were obtained:

	Liquid	Time of Flow at 25° C.
Toluene	33.8 sec.
Toluene solution of polymer	..	51.3 sec.

The dry co-polymer was a sticky mass which flowed slowly at room temperature, and could be handled with a spatula. It was too soft for satisfactory determination of Mooney value at 100° C. These properties are to be contrasted with those of GR-S synthetic rubber butadiene-styrene polymer, which is a tough elastic solid normally having a Mooney value of 45—55 at 100° C.

While this particular butadiene-styrene sub-rubbery co-polymer has been found in practice to give desirable results, many variations are possible to produce analogous useful base materials. The ratio between monomers may, for example, be considerably altered, although we have found that proportions of butadiene to styrene much lower than about 50 : 50 are less desirable for most uses, since such increased styrene content results in an undesirable reduction in the elasticity of the product.

For butadiene-styrene co-polymers prepared in emulsion form as hereinabove described, the addition of relatively large quantities of a suitable chain terminator, such as

dodecyl mercaptan, as a means of control of the extent of polymerization is generally preferred. (In the formula given, it may be noted that the use of but 0.6 parts by weight, i.e., less than one-third the stated quantity of dodecyl mercaptan, would result in the production of a typical rubbery co-polymer having a Mooney value in the range of 45—55 at 100° C.) Other reagents are known which function similarly in controlling polymer chain growth, and may replace the mercaptan; or other variations either in formula or procedure may be used in order to obtain the desired low polymer.

15 VULCANIZATION OF SUB-RUBBERY POLYMERS

As previously mentioned, vulcanization of the sticky sub-rubbery co-polymer is employed to transform it to a eucohesive pressure-sensitive tape adhesive which is more cohesive than adhesive.

A preferred method of vulcanization employs as the vulcanizing means an oil-soluble heat-advancing (heat-hardening) phenol-aldehyde resin. This type of phenol-aldehyde resin is rubber-reactive, is compatible with varnish drying oils (hence the "oil-soluble" designation), and hardens instead of softening when heated. It is thus to be distinguished from phenol-aldehyde resins which are oil-soluble but thermoplastic, or are heat-hardening but not oil-soluble. This type of phenol-aldehyde resin is well known, and is commonly formed of a para-substituted phenol reacted with formaldehyde (the latter being in excess of equimolecular amount) in the presence of an alkaline catalyst. "Bakelite" (Registered Trade Mark) No. BR—3360 and "Bakelite No. BR—14634", sold by the Bakelite Corporation, New York City, are commercially available examples. They are solid and brittle. These Bakelite resins are understood to be, respectively, para-phenyl-phenol and para-tertiary-butyl-phenol resins made with alkaline catalysts and with from 1.5 to 2 mols of formaldehyde for each phenol mol.

The following is given as an example of how such a resin can be made: Place one and one-half mols of formaldehyde (as a 40% solution) in an enamelled or glass reacting tank. Add one mol of para-tertiary-amyl-phenol. Then add, dissolved in a small amount of water, potassium hydroxide to the amount of one-half of one per cent of the total. Warm this mixture to 60° C. and hold at 60—80° C. until the free formaldehyde is 2% or less. Then add acetic acid to a pH of 4.5—5.5 (to neutralize the alkali); evaporate in vacuo to as heavy a body as practical to handle, and run out and cool.

It is also possible to use modified phenol-aldehyde resins. For example, a modified resin can be prepared by heating rosin with an equal weight of a neutral water-in-

soluble but still liquid resinous material formed by the partial reaction, in the presence of an alkaline catalyst, on one mol of phenol, four mols of para-tertiary-butyl phenol, and ten mols of formaldehyde. The resultant brittle solid resin acts both as a vulcanizing agent and as a tackifier resin.

The reaction between the sticky co-polymer and phenol-aldehyde resin is preferably performed in the presence of an activator, such as zinc oxide, zinc stearate or zinc resinate. Depending on the particular butadiene styrene-type co-polymer, and the degree of firmness desired in the pressure-sensitive tape adhesive product, and the degree of heating, the proportion of phenol-aldehyde resin may vary from as low as about 5 parts to as high as about 50 parts per 100 parts by weight of the polymer. The vulcanization effect depends in part upon the extent to which the reaction advances, since a larger proportion of phenol-aldehyde resin, partially reacted, will be equivalent to a smaller proportion which is more fully reacted. The extent of reaction completion depends upon the proportion, temperature and time, and proportion of activator. Thus it is possible to produce a eucohesive pressure-sensitive tape adhesive which is markedly thermo-setting, by using a larger proportion of partially reacted phenol-aldehyde resin, so that when tape made therewith is subjected to heating the adhesive will firm up to an even more highly cohesive state. This is an advantage for masking tapes and electrical coil tapes which may be subjected to baking after application. The absence of sulphur makes for a non-corrosive adhesive. A further advantage over sulphur vulcanization is that the adhesive does not soften even on very prolonged heating at high temperatures. The adhesive is also more resistant to organic solvents, and to the degradative effects of ultra-violet light.

The sulphur-type vulcanization procedure avoids the use of free sulphur and instead employs the thiuram-polysulfide accelerators, such as "Tetrone-A" (dipentamethylene-thiuram-tetrasulfide) and "Tuads" (Registered Trade Mark) (tetramethyl-thiuram-disulfide). These apparently liberate a nascent form of sulphur during the hot vulcanization process. There is no residual uncombined sulphur left over and after-vulcanization causing substantial tack-loss at room temperature is avoided. By employing an excess, the adhesive will be further vulcanized and firmed if and when the tape is subjected to heating. The proportion needed is small, varying in the range of about 1 to 5 parts by weight per 100 parts of the polymer, depending upon conditions. The activator can be zinc oxide, zinc stearate or zinc resinate, for example.

An example of a selenium-containing

self-vulcanizing organic accelerator of the thiuram-polysulfide type is "Selenae" (selenium diethyldithiocarbamate).

In any case, the amount of vulcanizing agent and extent of vulcanization are controlled so that the vulcanized adhesive product is, at room temperature, more cohesive than adhesive but still tacky and constitutes a stably tacky eucohesive pressure-sensitive tape adhesive.

A suitable general procedure is to mix together the sticky co-polymer, vulcanizing material, and activator and tackifier resin when used, in a heavy duty internal mixer provided with a jacket for heating (steam) and cooling (water). Mixing and heating are continued until the co-polymer mass has been vulcanized to the necessary extent. The reaction is discontinued by cooling the mixer, and termination can be hastened by adding solid- CO_2 ("dry ice") to the batch. An organic solvent, such as heptane, is then added to produce an adhesive solution having a coatable viscosity. This solution may be applied to tape backing sheeting in the usual way to produce, after drying out the solvent, pressure-sensitive adhesive sheeting, which can then be slit and wound into tape rolls. By dispersing the adhesive in a water vehicle, the use of an organic solvent can be avoided. Instead of being dispersed in a liquid vehicle, the adhesive may be applied directly by calendering or frictioning.

The end-point for the vulcanization reaction can be determined by a "smudge end-point" test. A small lump (5–10 grams) of the batch in the mixer is removed and is rolled and pressed on the surface of a clean glass plate. If no oiliness nor smudginess on the glass is produced, the end-point has been reached. By repeating this test at 5 minute intervals, the appearance of the desired degree of vulcanization can be readily detected. As the batch in the mixer approaches this smudge end-point, it increases in elasticity and cohesion to a point at which it pulls away from the revolving blades at each revolution. This change results in a distinct break in the curve of power-input (which can be followed with a watt meter) versus time substantially identical in time with the smudge end-point. Vulcanization can be carried beyond this end-point provided that it is not carried to a degree which will spoil the desired degree of tackiness of the adhesive at room temperature.

An alternative procedure is to mix the uncoagulated aqueous latex dispersion of the sub-rubbery polymer with an aqueous dispersion of the vulcanization agent and use this to coat tape backing sheeting. The coated sheet is heated to drive off the water and to cause the desired degree of vulcanization. Owing to the initial softness of the polymer

the intimate co-mingling of particles of compatible vulcanizing material, and the heating, a blending is produced which permits of the vulcanization of the sticky sub-rubbery polymer to a eucohesive pressure-sensitive tape adhesive. Tackifier resins and pigments (such as zinc oxide) in dispersed form can also be incorporated in the latex prior to coating. This procedure eliminates the mixing of the coagulated polymer and the use of organic solvent vehicles.

The following examples and accompanying description will further serve to illustrate the invention. All parts are by weight.

EXAMPLE 1.

Butadiene (75)—styrene (25) sub-rubbery polymer latex (36% solids)	700	
Alum (coagulant)	30	
Zinc oxide	100	85
Rosin (such as "Nelio (Registered Trade Mark) N" pale gum rosin, sold by the Glidden Co.)	2.5	
Soft thermoplastic terpene resin (soft as "Piccolyte S-25", sold by Pennsylvania Industrial Chemical Co.)	38	90
Oil-soluble heat-advancing phenol-aldehyde resin (such as "Bakelite BR-14634")	22	95
Solid- CO_2	150–200	
Heptane (volatile vehicle)	800–1000	
Alcohol (optional)	20	100

The latex, consisting of butadiene-styrene copolymerized in emulsion form in water to a sticky sub-rubbery state, was similar to that previously described. A portion of the coagulated polymer was tested for viscosity. A 0.98% solution in toluene had a flow time at 25° C. of 51.0 seconds in an Ostwald viscosimeter; the time for pure toluene being 33.8 seconds.

The aqueous latex was placed in a Baker-Perkins "Universal Mixing and Kneading Machine". The alum was added to coagulate the polymer, which thereupon adhered to the blades of the mixer. The liquid phase was decanted and the polymer was well washed with water, drained, and dried by heating in the mixer. The mixer was heated with steam in its jacket at 80 lbs. per sq. in. and the zinc oxide and resins were added in the order shown, each being well mixed in before the next was added. Heating (and mixing) was continued for about 1½ hours after the addition of the phenol-aldehyde resin, by which time the end-point was attained (as previously described) and the batch was then quickly cooled by passing cooling water through the jacket and rapidly

EXAMPLES 2 TO 6.

adding solid-CO₂ to the batch. The heptane and alcohol were then slowly added, with mixing, in amount sufficient to produce a viscous fluid having an apparent viscosity at 80° F. of 4000—5000 cps. when tested on a Brookfield "Synchro-Lectric" viscosimeter. The adhesive solution was withdrawn from the mixer and was ready for use in coating tape backings. The alcohol, serving as a viscosity reducer, can be omitted, an increased amount of heptane then being required to produce the same viscosity. This procedure results in a dispersion of the adhesive in heptane to facilitate coating. After coating and drying, the adhesive is however, highly resistant to softening by organic solvents, including heptane and gasoline.

When coated on a cellulose acetate cloth backing, an excellent non-corrosive pressure-sensitive electrical tape was produced. When this tape was used to anchor and to insulate the lead-in wires and other portions of the windings of radio coils wound with fine copper wire, there was no corrosion even though the coils were then heated for one hour at 250° F., and the adhesive did not soften. The tape held the wires firmly in place even when the coil was subsequently impregnated with hot wax.

By increasing the proportion of phenol-aldehyde resin in the above formula to 75 parts (30 parts per 100 parts of dry polymer) an adhesive was obtained which was pressure-sensitive but markedly thermo-setting. That is, when coated on a tape, the tape could be applied to a surface and when heated the adhesive firmed up greatly and increased its adhesive anchorage. However, the tape could then be stripped off without offsetting of adhesive.

These examples serve to illustrate the use of butadiene-styrene sub-rubbery co-polymers of varying degrees of polymerization and softness and the use of varying proportions of phenol-aldehyde resin and different reaction times.

In all cases the pressure-sensitive adhesive formulation was as follows:—

Dry butadiene (75)—styrene (25)	
sub-rubbery polymer	100
Zinc oxide	40
"Piccolyte S—25" (terpene tackifier resin)	15
Phenol-aldehyde resin	5-50
(Bakelite BR—14634)	(see table)

The procedure was as described in the preceding Example 1. In the following table the "Viscosity" of the polymer is given as the flow time for a given volume of toluene solution (of the stated polymer concentration) in an Ostwald viscosimeter, as compared to the calibration time of 33.8 seconds for pure toluene. Data is also given for the "Plastograph" readings (in meter-grams) of the dry polymers when tested in a Brabender Plastograph mixer; the lower the reading the greater the plasticity (softness). In contrast, ordinary GR—S butadiene-styrene synthetic rubber having a Mooney value of 45—55 at 100° C. gives a reading above 1000 (the scale of the Plastograph as here used did not extend beyond 1000). The "Conversion %" figures show the percentage of monomeric starting material that was converted to polymeric form in the making of the sub-rubbery polymer utilized.

Ex. No.	Polymer Properties				Parts of phenol-aldehyde resin	Reaction time (minutes)
	Conversion %	Plastograph reading	Viscosity % soln.	sec.		
2	75	306	1.04	60	5	39
3	75	306	1.04	60	10	17
4	75	306	1.04	60	50	38
5	58	125	1.13	50	10	55
6	40	40	0.98	45	10	90

In all cases excellent pressure-sensitive tape adhesives resulted, the degree of tackiness being greatest for Examples 3, 5 and 6. Tape made from adhesives of Examples 2, 3, 5 and 6 had excellent "wet-grab" and "soft-unwind" from rolls, meaning that the tape firmly bonded when a loop was lightly touched to a metal or glass surface without finger pressing, and that the tape unwound from rolls in an easy manner without jerking or sound. The adhesive of Example 4 was much firmer (notice the much larger proportion of phenol-aldehyde resin) and had a more resinous characteristic. The tackifier resin, when used, may be added in whole or part after the reaction, in

connection with mixing the adhesive in the solvent. However, it is preferred to blend the tackifier resin and sticky polymer prior to vulcanization as this results in an adhesive wherein the tackifier resin is more homogeneously held and there is much less tendency for it to bleed out when the adhesive is subjected to organic solvents, oils or waxes, or is heated. When an excess of vulcanizing agent is used (to produce an adhesive which will have marked thermo-setting properties), the excess may if desired be incorporated into the adhesive following the adhesive-making vulcanization reaction, although this is not generally the preferred practice.

In the foregoing examples, the formulations have included tackifier resin and zinc oxide. The zinc oxide serves as an activator and also constitutes a reinforcing and opacifying pigment. These are not essential. The zinc oxide can be reduced to a small proportion serving essentially merely as an activator (as in making transparent adhesives). It can be entirely omitted, although this is not recommended since the rate of vulcanization is thereby considerably decreased. Equivalent vulcanization activators can be used in place of zinc activators, as well known in the vulcanization art; for example, magnesium activators can be used. The tackifier resin can be omitted, and sufficient tackiness then obtained merely by the inherent tackiness of the vulcanized sticky polymer. Various compatible tackifier resins can be used, such as rosin, zinc resinate, ester gum, terpene resins and hydrogenated indene resin. Starch and clay are examples of extenders which can be used if desired.

In the foregoing examples, the blend of sub-rubbery polymer and phenol-aldehyde resin has been reacted in the mixer, and then mixed with solvent to produce a finished adhesive in solution form.

However, the mixture can be reacted *in situ* in the product of which the adhesive is to be a part. Thus the mixture in unreacted form can be readily coated or spread upon sheet material, particularly if a fluid polymer is employed, followed by heating to cause the necessary vulcanization for obtaining a eucohesive pressure-sensitive adhesive state. Cloth, felted fabrics, and porous paper, can be saturated or impregnated with the unreacted mixture, so that the final adhesive will penetrate the sheeting and unify the fibers. A long-fibered hemp tissue paper (such as "Troya Tissue") can be passed through a body of the unreacted mixture of co-polymer and resin and thence through an orifice so as to saturate the paper and coat it on both sides, followed by heating to produce a eucohesive pressure-sensitive adhesive. Double-coated tape of

this kind can be mounted on a removable liner to permit winding in rolls, and has many uses. The double-coated tissue can be laminated to a permanent backing, such as a film of cellophane or cellulose acetate, or a metal foil, the vulcanization heating being performed either before or after lamination, to produce a reinforced film-backed pressure-sensitive tape. The viscosity of the unreacted polymer-resin mixture can be reduced by mixing with a volatile vehicle, such as heptane, to facilitate coating and impregnation, subsequent heating drying out the vehicle.

EXAMPLE 7.

This example illustrates the use of a thiuram-polysulphide vulcanizing agent in place of the phenol-aldehyde resin of the preceding examples. The compounding formulation was:

Sub-rubbery co-polymer of butadiene (75)—styrene (25)	100
Zinc oxide	40
Rosin	1
"Piccolyte S—25" (terpene tackifier resin)	15
"Tetrone A" (dipentamethylene - thiuram - tetra-sulphide)	1.2

The compounding procedure and the viscosity of the polymer was substantially the same as is described in Example 1, except for the use of the different vulcanizing agent. The mixer was heated with jacket steam of about 80 lbs. per sq. in. pressure and the end-point was determined by the smudge test, which was reached upon 48 minutes heating after addition of the "Tetrone A". Cooling was accomplished in the same way and the adhesive was dispersed in a volatile vehicle by mixing in sufficient heptane and alcohol to produce a coatable viscosity.

When coated upon tape backings there were produced excellent pressure-sensitive adhesive tapes. When samples of the tape were applied to a steel plate and heated it was found that the adhesive remained firm (for example, when heated for four hours at 220° F.), showing that the adhesive is of the non-thermoplastic type. The adhesive was stably tacky at room temperatures.

What we claim is:—

1. A method of producing a stably tacky eucohesive pressure-sensitive adhesive useful in adhesive tapes which comprises heating a sub-rubbery butadiene-styrene co-polymer with an oil-soluble heat-advancing phenol-aldehyde resin or a self-vulcanizing organic accelerator of the thiuram-polysulfide type to a stage at which the product is more cohesive than adhesive but still tacky, the product being substantially free from after-vulcanization and tack-loss at room temperatures.

2. A method according to Claim 1 which comprises heating the butadiene-styrene co-polymer with the phenol-aldehyde resin or accelerator of the thiuram-polysulfide type and a minor proportion of a compatible tackifier resin.

3. A normally and stably tacky eucohesive pressure-sensitive adhesive tape consisting of a backing coated or impregnated with an adhesive comprising a sub-rubbery butadiene-styrene polymer which has been heated with an oil-soluble heat-advancing phenol-aldehyde resin or a self-vulcanizing organic accelerator of the thiuram-polysulfide type to a stage at which the product is more cohesive than adhesive but stably tacky at room temperatures, and which is substantially free from after-vulcanization and tack-loss at room temperatures.

4. An adhesive according to Claim 3 containing a minor proportion of a compatible tackifier resin.

5. An adhesive according to Claim 3 or Claim 4 wherein said adhesive contains an excess of unreacted heat-vulcanizing agent adapted to additionally firm-up the adhesive

and when subjected to an elevated temperature.

6. A pressure-sensitive adhesive sheet or tape characterized by having a coating of the adhesive specified in Claim 3, 4 or 5.

7. A method of producing a stably tacky eucohesive pressure-sensitive adhesive useful in adhesive tapes substantially as herein described.

8. A normally and stably tacky eucohesive pressure-sensitive tape adhesive substantially as herein described.

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